Investigation of Mechanism of Electrochemical Corrosion of Graphite Electrodes

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Graphite electrodes can find in principle enough wide application as electrodes for some types of rechargeable batteries and supercapacitors, electrosorption/desorption electrodes, anodes in different processes of electrochemical synthesis, etc. Nevertheless, the corrosion processes during anodic polarization of such electrodes are the main limitation for their practical using.

We have performed comparative electrochemical investigation of properties electrodes, obtained from various types of initial natural and artificial graphite. The special electrochemical method of prolonged sequential cyclic voltammetry was proposed for an evaluation of graphite stability to oxidation.

There is exists point of view that the main mechanism of electrochemical corrosion connected with a full step by step oxidation of graphite to CO_2 during the cycling.

For studying the possible mechanisms of electrochemical corrosion we have compared first of all the capacity loss for graphite electrodes with the loss of their mass during prolonged galvanostatic cycling for the natural Zavalievo graphite (NGZ, Ukraine) and the natural graphite flakes «Kropfmuhl Normalflocke» (NGF, Germany). Furthermore, thermally expanded graphite (TEG), manufactured in Superior Graphite Co. (Chicago) was tested.

The comparison of electrode capacity loss with loss of their mass during the cycling unambiguously shows, that degradation of electrical characteristics cannot be explained only by CO_2 derivation with appropriate decrease of an active material store. The main mechanism depends strongly on the type of graphite.

For example, for NGZ the loss of capacity is higher but comparable with the loss of graphite mass (66.8 and 50.0%). Thus, corrosion mechanism connected with CO_2 derivation is predominant for such non stable to oxidation graphite group.

For NGF the loss of capacity is much more higher (of about 68%) than the loss of graphite mass (of about 2.5%). Thus, for such type of graphite, as well as for TEG, the corrosion mechanisms connected with formation of OH^- and COOH- surface groups are predominant.

The minimal resistance to oxidation (few dozens of cycles) is demonstrated by the natural Zavalievo graphite. Natural graphite flakes «Kropfmuhl Normalflocke» prove to possess significantly higher resistance to oxidation (up to 100 cycles). Furthermore, TEGs demonstrate even much higher resistance to oxidation (250 cycles).

The main reason of graphite electrodes corrosion for NGF and TEG is the derivation and accumulation of surface groups, which graduallies lock "entrances" and hinder intercalation of anions in interlayer space. The evaluations show that the most probable areas, where the redundant acid centers are located, are the initial sites and "entrances" in interlayer space.

The use of new types of graphite, more proof to oxidation, (in particular, thermally expanded graphite) can largely hinder such passivation effect to increase the resistance for corrosion.

Quite high resistivity and stability create real prerequisites for enough wide application of such graphite materials.